

## CRUDE OIL DESULFURIZATION

### FIELD OF THE INVENTION

The present invention is directed to a method for hydrodesulfurizing crude oil.

### BACKGROUND OF THE INVENTION

Crude oil is conventionally processed by distillation followed by various cracking, solvent refining and hydroconversion processes to produce a desired slate of fuels, lubricating oil products, chemicals, chemical feedstocks and the like. An example conventional process includes distillation of a crude oil in an atmospheric distillation column to form a gas oil, naphtha, a gaseous product, and an atmospheric residuum. Generally, the atmospheric residuum is further fractionated in a vacuum distillation column to produce a vacuum gas oil and a vacuum residuum. The vacuum gas oil is usually cracked to more valuable light transportation fuel products by fluid catalytic cracking or hydrocracking. The vacuum residuum may be further treated to recover a higher amount of useful products. Such upgrading methods may include one or more of, for example, residuum hydrotreating, residuum fluid catalytic cracking, coking, and solvent deasphalting. Streams recovered from crude distillation at the boiling point of fuels have characteristically been used directly as fuels.

U.S. Patent No. 4,885,080 teaches preparing a synthetic crude oil by fractionating a heavy crude oil, hydrodesulfurizing the distillate cut, hydrodemetallizing the residuum and combining the hydrotreated cuts with a third liquid fraction to form the synthetic crude oil. U.S. Patent No. 3,830,731 teaches distilling a heavy hydrocarbon feedstock into a vacuum gas oil and a vacuum residuum fraction, and hydrodesulfurizing each fraction.

16 Thus, in response to these tightening regulations, refiners have constructed  
17 separate hydroprocessing units to upgrade each of the fuel streams produced  
18 in the refinery. The net effect is a large number of similar processing units,  
19 each handling a separate stream, requiring additional tankage and operators.  
20 Specific streams are alternatively heated for reaction or fractionation, and  
21 then cooled for separation and storage. Multiple reaction systems requires  
22 multiple hydrogen supply, pressurization and distribution systems. It is  
23 desirable to have a process for hydroprocessing the entire crude oil into  
24 useful low aromatic, low sulfur products while significantly reducing the  
25 number of refinery processing steps and processing equipment required to  
26 convert the crude to useful products. Such a process is the subject of the  
27 present invention.

29 In U.S. Patent No. 5,009,768, a complete crude or the atmospheric and  
30 vacuum residues thereof mixed with vacuum gas oils is demetallized and the  
31 demetallized product hydrotreated for hydrodenitrogenation and  
32 hydroconversion. In U.S. Patent No. 5,382,349, a heavy hydrocarbon oil is  
33 hydrotreated, the hydrotreated oil distilled and a vacuum residue thermally  
34 hydrocracked in a slurry bed. U.S. Patent No. 5,851,381 provides a method

1 of refining crude oil by distillation and desulfurization. In the method, a  
2 naphtha fraction is separated from crude oil by distillation, with the remaining  
3 residual fraction after the naphtha fraction has been removed from the crude  
4 oil being hydrodesulfurized and the hydrodesulfurized fraction separated into  
5 further fractions, first in a high pressure separator and then by atmospheric  
6 distillation. A residue is further upgraded in a residue fluid catalytic cracking  
7 process.

#### 8 9 SUMMARY OF THE INVENTION

10  
11 In the present process, a crude oil feed is desulfurized and processed  
12 (hydrotreated and hydrocracked) to form low sulfur, low aromatic fuels in an  
13 integrated unit, with a single hydrogen supply and recovery loop, with minimal  
14 cooling of intermediate products, and without tank storage of intermediate  
15 products. The integrated unit comprises a series of catalytic reaction zones,  
16 each containing a single catalyst or a layered catalyst system selected for a  
17 particular application, whether it be desulfurization of a crude feed,  
18 hydrocracking a gas oil stream or hydrotreating a particular stream to reduce  
19 the aromatic and/or sulfur content of the stream to low levels. Flash  
20 separation of reaction products exiting a particular catalytic reaction zone is  
21 tailored to isolate hydrogen with minimal heat exchange beyond that required  
22 to prepare the reaction products for the next processing step.

23  
24 In the present invention, a crude oil feed is passed directly to a crude  
25 desulfurization unit for desulfurization. The crude oil feed may be desalted  
26 and volatile materials removed prior to desulfurization, but a substantial  
27 portion of the crude oil feed is subjected to desulfurization in a desulfurization  
28 reaction zone. A number of reactions is expected to occur during the  
29 desulfurization process. Portions of the crude oil feed which contain  
30 metal-containing components will be at least partially demetallized during the  
31 desulfurization process. Likewise, nitrogen and oxygen are removed, along  
32 with sulfur, during the desulfurization process. While the amount of cracked  
33 products produced during desulfurization will be relatively small, some amount





DESCRIPTION OF THE FIGURES

Figure 1 discloses a crude oil desulfurization process which comprises the following steps:

- a) hydrodesulfurizing a crude oil feed in a crude desulfurization unit;
- b) separating the desulfurized crude oil and recovering a light gas oil fraction, a vacuum gas oil fraction and a vacuum residuum fraction;
- c) hydrocracking the vacuum gas oil to form at least one low sulfur fuel product; and
- d) hydrotreating the light gas oil fraction.

Figure 2 discloses a crude oil desulfurization process which comprises the following steps:

- a) hydrodesulfurizing a crude oil feed;
- b) separating the desulfurized crude oil and recovering at least a light gas oil fraction, a vacuum gas oil fraction and a residual fraction;
- c) hydrocracking the vacuum gas oil in a first hydrocracking reaction zone to reduce the sulfur content and the nitrogen content therefrom and to produce a low sulfur gas oil product;
- d) hydrocracking the low sulfur gas oil product in a second hydrocracking reaction zone at a conversion of at least 20% to form at least one low sulfur fuel product; and
- e) hydrotreating the light gas oil fraction.

For the purposes of this specification, the term "middle distillates" as used herein is to be taken as a reference to hydrocarbons or hydrocarbon mixtures having a boiling point or boiling point range substantially corresponding to that of the kerosene and diesel fractions obtained during the conventional atmospheric distillation of crude oil feed. The term "light gas oil" (LGO) as used herein is to be taken as a reference to hydrocarbons or hydrocarbon mixtures which are isolated as distillate streams obtained during the conventional atmospheric distillation of a refinery stream, a petroleum stream or a crude oil stream. The term "vacuum gas oil" (VGO) as used herein is to be taken as a reference to hydrocarbons or hydrocarbon mixtures which are isolated as distillate streams obtained during the conventional vacuum distillation of a refinery stream, a petroleum stream or a crude oil stream. The term "naphtha" as used herein is a reference to hydrocarbons or hydrocarbon mixtures having a boiling point or boiling point range substantially corresponding to that of the naphtha (sometimes referred to as the gasoline) fractions obtained during the conventional atmospheric distillation of crude oil feed. In such a distillation, the following fractions are isolated from the crude oil feed: one or more naphtha fractions boiling in the range of from 30 to 220°C, one or more kerosene fractions boiling in the range of from 120 to 300°C and one or more diesel fractions boiling in the range of from 170 to 370°C. The boiling point ranges of the various product fractions isolated in any particular refinery will vary with such factors as the characteristics of the crude oil source, refinery local markets, product prices, etc. Reference is made to ASTM standards D-975 and D-3699-83 for further details on kerosene and diesel fuel properties. The term "hydrocarbon fuel" is to be taken as a reference to either one or a mixture of naphtha and middle distillates. Unless otherwise specified, all distillation temperatures listed herein refer to normal boiling point and normal boiling range temperatures. By "normal" is meant a boiling point or boiling range based on a distillation at one atmosphere pressure, such as that determined in a D1160 distillation.





FIGURE 1  
REACTOR CONFIGURATION

Referring now to Fig. 1, a crude oil feed **02** is passed to a crude desulfurization unit **04** in combination with a hydrogen rich stream **44** for hydrodesulfurizing the crude oil feed. Crude desulfurization unit **04** comprises one or more reaction zones, each of which contains one or more catalyst beds. The crude desulfurization unit removes a substantial portion of the contaminants present in the crude oil feed, including metals, sulfur, nitrogen and Conradson carbon. Catalysts provided in crude desulfurization unit **04** for removing these contaminants may include a single catalyst or a layered catalyst system comprising multiple catalysts present in one or more reactors. When using a reaction train comprising more than one reactor in series operation, a major portion, if not all, of the liquid product from each reactor (except the last reactor vessel in the reaction train) is passed to a next reactor for additional processing. In the layered catalyst system, catalysts are pre-selected for their intended specific use, whether it be demetallation, or sulfur and nitrogen removal, or asphaltene and Conradson carbon removal, or mild conversion. Different catalyst layers may also be selected to facilitate the desulfurization of various boiling point fractions present in the crude oil feed, including naphtha fractions, middle distillate fractions, vacuum gas oil fractions and/or residuum fractions.

DESULFURIZATION UNIT CATALYST

Catalysts for use in the crude desulfurization unit **04** are generally composed of a hydrogenation component, selected from Group VIb (preferably molybdenum and/or tungsten, more preferably molybdenum) and Group VIII (preferably cobalt and/or nickel) of the Periodic Table, or a mixture thereof, all supported on an alumina support. Phosphorous (Group Va) oxide is optionally present as an active ingredient. A typical desulfurization catalyst contains from 3 to 35 wt% hydrogenation components, with an alumina binder.

1 The catalyst pellets range in size from 1/32 inch to 1/8 inch. A spherical,  
2 extruded, trilobate or quadrilobate shape is preferred. In general, the crude oil  
3 feed passing through the desulfurization unit contacts first a catalyst  
4 preselected for metals removal, though some sulfur, nitrogen and aromatic  
5 removal will also occur. Subsequent catalyst layers are preselected for sulfur  
6 and nitrogen removal, though they would also be expected to catalyze the  
7 removal of metals and/or cracking reactions.

8  
9 Catalyst layer(s) preselected for demetallization comprise catalyst(s) having  
10 an average pore size ranging from 125 to 225 Å and a pore volume ranging  
11 from 0.5 - 1.1 cm<sup>3</sup>/g. Catalyst layer(s) preselected for  
12 denitrification/desulfurization comprise catalyst(s) having an average pore  
13 size ranging from 100 to 190 Å with a pore volume of 0.5 - 1.1 cm<sup>3</sup>/g.  
14 U.S. Patent No. 4,90,243 describes a hydrotreating catalyst having a pore  
15 size of at least about 60 Å, and preferably from about 75 Å to about 120 Å. A  
16 demetallation catalyst useful for the present process is described, for  
17 example, in U.S. Patent No. 4,976,848, the entire disclosure of which is  
18 incorporated herein by reference for all purposes. Likewise, catalysts useful  
19 for desulfurization of heavy streams are described, for example, in  
20 U.S. Patent No. 5,215,955 and U.S. Patent No. 5,177,047, the entire  
21 disclosures of which is incorporated herein by reference for all purposes.  
22 Catalysts useful for desulfurization of middle distillate, vacuum gas oil streams  
23 and naphtha streams are described, for example, in U.S. Patent  
24 No. 4,990,243 the entire disclosures of which are incorporated herein by  
25 reference for all purposes.

#### 26 27 REACTION CONDITIONS 28

29 It is desirable that the crude desulfurization unit **04** be controlled to maintain  
30 the product sulfur at a specified maximum concentration. For example, when  
31 the product sulfur is maintained at less than 1 wt% based on feed, and  
32 preferably less than 0.75 wt% based on feed, reaction conditions in the crude  
33 desulfurization unit **04** include a reaction temperature between about 315°C  
34 and 440°C (600°F – 825°F), pressures from 6.9 MPa to about 20.7 MPa

1 (1000 - 3000 psi), and a feed rate (vol oil/vol cat hr) from 0.1 to about 20 hr<sup>-1</sup>.  
2 Hydrogen circulation rate are general in the range from about 303 std liter  
3 H<sub>2</sub>/kg oil to 758 std liters H<sub>2</sub>/kg oil (2000-5000) standard cubic feet per barrel).

#### 5 DESULFURIZED CRUDE OIL PROPERTIES

7 The crude oil desulfurization process removes greater than 25% w/w,  
8 preferably greater than 50% w/w of the sulfur present in the crude oil feed 02.  
9 The preferred desulfurized crude oil 06 typically has a sulfur content of less  
10 than 1 wt%, preferably less than 0.75 wt%, still more preferably less than  
11 0.5 wt%.

#### 12 DESULFURIZED CRUDE DISTILLATION

14 Unreacted hydrogen isolated from crude desulfurization unit 04 is separated  
15 from desulfurized crude oil 06 in one or more flash zones 08 (e.g. a  
16 desulfurization unit high pressure separator) and the resultant desulfurized  
17 liquid 10 is passed to crude fractionator 12 for fractionation to produce at least  
18 a light gas oil fraction 20, a vacuum gas oil fraction 18 and a residuum  
19 fraction 16. Crude fractionator 12 is a single or multiple column fractionation  
20 system, and preferably a two column or stage fractionator. One example two-  
21 stage fractionator comprises an atmospheric distillation column operated  
22 substantially at or slightly above atmospheric pressure, and a vacuum  
23 distillation column operated at sub-atmospheric pressure. Such distillation  
24 column systems are well known. In a preferred process of the invention,  
25 desulfurized liquid 10 is passed from flash separation zone(s) 08 directly to  
26 crude fractionator 12 without cooling desulfurized liquid 10 beyond that  
27 required for the distillation in crude fractionator 12. The temperature of  
28 stream 10 passing from 8 to 12 is preferably maintained at a temperature of at  
29 least 250°F, and preferably of at least 600°F. In the embodiment illustrated in  
30 Fig. 1, all of the desulfurized crude oil, absent light gases, are passed to crude  
31 fractionator 12 for fractionation.

## HYDROCRACKING UNIT

The vacuum gas oil fraction **18** from the crude fractionator **12** is passed to the hydrocracking unit **54**, preferably directly, without tankage and with minimal heat removal, for further processing to produce low sulfur and low aromatic hydrocarbon fuels. The hydrocracking unit **54** contains catalyst selected for further removal of sulfur and nitrogen compounds, for saturation and removal of aromatic compounds, and for cracking for molecular weight reduction. For the present invention, conversion is generally related to a reference temperature, such as, for example, the minimum boiling point temperature of the hydrocracker feedstock. The extent of conversion relates to the percentage of feed boiling above the reference temperature which is converted during hydrocracking into hydrocrackate boiling below the reference temperature. Where the reference temperature is selected to be, e.g. 370°C (700°F), overall conversion during hydrocracking in hydrocracking unit **54** is typically greater than 10%, and preferably greater than 20%.

## 2ND STAGE PRODUCT

Effluent from hydrocracking unit **54** is separated in one or more flash separation units **28** (e.g. hydrocracker separation unit) to isolate at least a hydrocracked liquid product **62**, which is passed to product fractionator **30** for fractionation. In the preferred process, recycle H<sub>2</sub> stream **56** is separated from hydrocracked effluent **52** for recycle to various units in the integrated process, and the remaining liquid **62** is passed to a product fractionator **30** for isolating fuel product(s). The purity of recycle H<sub>2</sub> stream **56** will generally be maintained at greater than 75 mole% hydrogen. In order to maintain energy efficiency, hydrocracked liquid product **62** is passed to fractionator **30** without substantial cooling of **62**. At least one fuel product, **40**, is isolated from product fractionator **30**.





## HYDROGEN RECOVERY

The hydrogen stream **14** isolated from flash separation zone **08** may be further purified in, for example, an amine scrubber **46** to remove some or all of the  $H_2S$  and  $NH_3$  gases. Following compression, the purified hydrogen is passed to the first hydrocracker stage **22** and the second hydrocracker stage **26**.

### 1ST STAGE

Reaction in first hydrocracker stage **22** is maintained at conditions sufficient to further remove nitrogen and sulfur contaminants from the vacuum gas oil feed **18** and for reducing the aromatic content of the vacuum gas oil feed **18**.

These hydrotreating reactions are generally characterized by a low amount of conversion, e.g. less than 20%, preferably less than 15%. In general, it is desirable to lower the nitrogen content of the hydrocarbon feedstock stream to less than 50 parts per million by weight (ppm), preferably less than about 10 ppm and for increased catalyst life to a level of less than 2 ppm or even as low as about 0.1 ppm. Similarly, it is generally desirable to lower the sulfur content of the hydrocarbon feedstock stream to less than about 0.5% by weight percent, preferably less than about 0.1%, and in many cases as low as about 1 ppm.

### 1ST STAGE CONDITIONS

Thus, the one or more reaction zones in first hydrocracker stage **22** are operated at reaction temperatures between 250°C and about 500°C ( 482 - 932°F ), pressures from 3.5 MPa to about 34.2 MPa (500 - 3500 psi) , and a feed rate (vol. oil/vol. cat h) from 0.1 to about 20hr<sup>-1</sup> . Hydrogen circulation rates are in general in the range from about 350-std. liter H<sub>2</sub>/kg oil to 1780 H<sub>2</sub>/kg oil (2310 - 11750 standard cubic feet per barrel). Preferred reaction temperatures range from 340°C to about 455°C ( 644 - 851°F ). Preferred total reaction pressures range from 7.0 MPa to about 20.7 MPa (1000 - 3000 psi ).

## 1ST STAGE CATALYST

Catalysts useful in first hydrocracker stage **22** generally contain at least one Group VIb metal (e.g. molybdenum) and at least one Group VIII metal (e.g. nickel or cobalt) on an alumina support. A phosphorous oxide component and a cracking component, such as silica-alumina and/or a zeolite, may also be present. A layered catalyst system may also be used, e.g. the layered catalyst system taught in U.S. Patent No. 4,990,243, which is incorporated herein by reference for all purposes. The catalyst selected for use in first hydrocracker stage **22** will generally have a pore volume in the range of 0.5 to 1.2 cm<sup>3</sup>/g, with an average pore diameter of between 100 Å and 180 Å, and a surface area 120 and 400 m<sup>2</sup>/g, wherein at least 60% of the pores have a pore diameter of more than 100 Å. The first stage catalyst could also be a layered system of hydrotreating and hydrocracking catalysts. The preferred catalyst for first hydrocracker stage **22** comprises a nickel molybdenum or cobalt molybdenum hydrogenation component and a silica-alumina component with an alumina binder.

## HOT H<sub>2</sub> STRIPPER

The effluent **48** from the first hydrocracking stage **22** contains unreacted hydrogen, gaseous and liquid products. Hydrogen isolated from effluent **48** contains H<sub>2</sub>S and NH<sub>3</sub>. In conventional processes, such hydrogen is purified prior to use as recycle to the first hydrocracking stage or as H<sub>2</sub> feed to the second hydrocracking stage. The present process is based on the realization that hydrogen isolated from effluent **48** is suitable for use as H<sub>2</sub> feed to the crude desulfurization unit **04**, without extensive purification. The use of hydrogen in this way is facilitated by passing effluent **48** to hot hydrogen stripper **24** for removing light gases contained therein, including hydrogen and light hydrocarbon gases, using heated hydrogen **36**. Typically, hot hydrogen stripper **24** is operated at temperatures preferably between 260°C and 399°C (500°F and 750°F). Hydrogen-rich stream **44**, which is isolated from hot hydrogen stripper **24**, is combined with crude oil feed **02**, preferably with no further purification, for desulfurizing crude oil feed **02** in crude desulfurization





## 2ND STAGE CATALYST

The catalyst used in the second hydrocracking stage **26** is a conventional hydrocracking catalyst of the type used to carry out hydroconversion reactions to produce transportation fuels. First hydrocracker stage **22** and second hydrocracker stage **26** can contain one or more catalyst in more than one reaction zone. If more than one distinct catalyst is present in either or the reaction zones, they may either be blended or be present as distinct layers. Layered catalyst systems are taught, for example, in U.S. Patent No. 4990243. Hydrocracking catalyst useful for second hydrocracker stage **26** are well known. In general, the hydrocracking catalyst comprises a cracking component and a hydrogenation component on an oxide support material or binder. The cracking component may include an amorphous cracking component and/or a zeolite, such as a Y-type zeolite, and ultrastable Y type zeolite, or a dealuminated zeolite. Particularly preferred catalytic cracking catalysts are those containing at least one zeolite which is normally mixed with a suitable matrix such as alumina, silica or silica-alumina. A suitable amorphous cracking component is silica-alumina. The preferred amorphous cracking component is between 10 and 90 weight percent silica, preferably between 15 and 65 weight percent silica, the remainder being alumina. A cracking component containing in the range from about 10% to about 80% by weight of the Y-type zeolite and from about 90% to about 20% by weight of the amorphous cracking component is preferred. Still more preferred is a cracking component containing in the range from about 15% by weight to about 50% by weight of the Y-type zeolite, the remainder being the amorphous cracking component. Also, so-called x-ray amorphous zeolites (i.e., zeolites having crystallite sizes too small to be detected by standard x-ray techniques) can be suitably applied as cracking components. Hydrogenation components suitable for the hydrocracking and/or hydrotreating catalysts which are used in the present integrated process include those which are comprised of at least one Group VIII (IUPAC Notation) metal, preferably iron, cobalt and nickel, more preferably cobalt and/or nickel and at least one Group VI (IUPAC Notation) metal, preferably molybdenum and tungsten, on a high surface area support

material, preferably alumina. Other suitable catalysts include zeolitic catalysts, as well as noble metal catalysts where the noble metal is selected from palladium and platinum. It is within the scope of the present invention that more than one type of catalyst be used in the same reaction vessel. The Group VIII metal is typically present in an amount ranging from about 2 to about 20 weight percent. The Group VI metal will typically be present in an amount ranging from about 1 to about 25 weight percent. The hydrogenation components in the catalyst may be in the oxidic and/or the sulfidic form. If a combination of at least a Group VI and a Group VIII metal component is present as (mixed) oxides, it will be subjected a sulfiding treatment prior to proper use in hydrotreating or hydrocracking. Suitably, the catalyst comprises one or more components of nickel an/or cobalt and one or more components of molybdenum and/or tungsten or one or more components of platinum and/or palladium. Catalysts containing nickel and molybdenum, nickel and tungsten, platinum and/or palladium are particularly preferred.

The effective diameter of the zeolite catalyst particles are in the range of from about 1/32 inch to about 1/4 inch, preferably from about 1/20 inch to about 1/8 inch. The catalyst particles may have any shape known to be useful for catalytic materials, including spheres, cylinders, fluted cylinders, prills, granules and the like. For non-spherical shapes, the effective diameter can be taken as the diameter of a representative cross section of the catalyst particles. The catalyst particles will further have a surface area in the range of from about 50 to about 500 m<sup>2</sup>/g.

#### LAYERED HYDROCRACKING ZONE FOR LIGHT GAS OIL HYDROTREATING

In Fig. 1, a light gas oil stream **20** isolated from the desulfurized liquid **10** is hydrotreated in **58** to remove sulfur and/or aromatics in preparation of a low sulfur, low aromatic fuel product **60**. In a separate preferred embodiment illustrated in Fig. 2, the hydrotreating catalyst useful for hydrotreating light gas oil stream **20** is layered at or near the bottom of second hydrocracker stage **26**. Thus, second hydrocracker stage **26** includes a layered catalyst system,



